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(54) Title: POWDER COATING COMPOSITION (57) Abstract The present invention discloses a method for the preparation of heat-resistant protective coatings wherein powder-based compositions are cured at temperatures greater than about 190 °C to form high-film-build coatings which are substantially free of coating defects, said composition comprising a polyacrylic polymer (preferably a glycidyl-functional polyacrylic polymer), a hydroxyl-substituted polysiloxane and a metal or metal oxide, and preferably an inorganic compound which is not a metal or metal oxide (such as a silicate).		

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POWDER COATING COMPOSITION

Cross-Reference To Related Application

This application is a Continuation-In-Part of copending application U.S. Serial
5 No. 08/960,045, filed October 29, 1997, Pending; which is a Continuation-In-Part of
U.S. Serial No. 08/751,599, issued November 4, 1997; which is a Continuation-In-Part of
U.S. Serial No. 08/567,498, filed December 4, 1995, abandoned; which applications are
incorporated herein by reference.

10 Field Of The Invention

The present invention relates to a thermoforming heat-resistant powder coating
composition having high heat resistance. Specifically, the present composition provides
a coating that can be applied at high-film-build to articles. More specifically, it relates to
a method wherein powder-based compositions are applied at a high-film-build and cured
15 at temperatures greater than about 190°C or greater than about 205°C to form protective
coatings which are substantially free of coating defects. Still more particularly, the
present invention relates to powder-based compositions which can be applied at high
film build, cured at temperatures greater than about 190°C or greater than about 205°C to
form protective coatings which are substantially free of coating defects, and which
20 display improved thermal resistance to temperatures preferably up to and above about
370°C, 425°C, 480°C or 540°C.

Background Of The Invention

Powder coating compositions are well known in the established art. A variety of
25 articles are routinely powder coated by dipping, or tumbling them in a suspended or
static bed of resinous powder coating or by spray or sprinkling. The article on which the
coating is applied is then heated to form a cured powder coating. These coatings have
been shown to be particularly useful on metal surfaces including steel, aluminum and
iron.

30 Various powder coating compositions are available that have been used in heat-
resistant applications. For example, it is known in the art that aromatic epoxy resins are

used to provide good heat resistance. Epoxy compositions or epoxy and silicone mixtures have also been used in the industry for the same purpose. An example of a silicone coating composition is shown in U.S. Patent No. 5,433,396 (Daly et al.).

However, this composition, along with the other silicone based powder coating
5 compositions, relies on the condensation of the silicone resin with another resin or itself to form the coating composition.

Additional references which describe the preparation of heat-resistant protective coatings are described below:

U.S. Patent No. 4,877,837 (Reising et al.) discloses powder-based compositions
10 comprising glycidyl functional acrylic polymers admixed with silicone having hydroxyl functional groups. The compositions may contain additives such as flow agents, outgas agents and filler pigments (i.e., clay, tile, silica, hydrated silicates of aluminum and calcium metasilicate) and are cured at a temperature between 180°C - 200°C).

U.S. Patent No. 4,446,259 (Vasta) discloses coating compositions in a liquid
15 carrier, which can be cured at ambient temperatures, comprising glycidyl functional acrylic polymers admixed with a reactive polysiloxane. The coatings may contain additives such as metal oxides, metallic pigments and trace amounts of multivalent metal ions including tin and zinc. Vasta also discloses fluorocarbon-based powder compositions which are baked at 200°C - 345°C for about 2 hours to provide a coating
20 25-75 microns thick.

Other related patents include: U.S. Patent No. 4,404,042 (Okada et al.); U.S. Patent Nos. 4,657,963 and 4,746,568 (Matsumoto et al.); U.S. Patent No. 5,442,396 (Daly et al.); U.S. Patent No. 4,879,344 (Woo et al.); and U.S. Patent No. 5,087,286 (Fukuda et al.).

25 A drawback with the prior art coating references is that they do not possess high heat resistance. For example, when said compositions are cured at elevated temperatures, condensation and thermal decomposition by-products often generate gases which can form pinholes, cracks and craters in the protective coatings. These defects can be detrimental to coating properties including aesthetics, heat resistance and corrosion
30 resistance and typically limit the coating thickness to less than about 100 microns.

To enhance the performance characteristics of protective coatings, it is often necessary to apply a high-film-build. A higher-film-build generally allows complete

deposition of the powders on a substrate and once cured, it increases the protective coating's barrier of protection. These prior art coatings are not conducive for high film thicknesses.

Therefore, there remains a need for powder-based coating compositions which are capable of providing heat-resistant protective coatings which may have a film thickness greater than about 100 microns, are substantially free of coating defects, and display improved high temperature durability.

Summary Of The Invention

The invention discloses a thermoforming powder coating composition comprising a ceramic additive for use on metal substrates including steel, aluminum, iron and the like. Ceramic additives include inorganic oxide and/or metal. The presence of the inorganic oxide and/or metal additive to the starting composition has extended the time and the temperature to which the composition may be subjected without thermal degradation, either at low film thickness, and particularly when making high film thickness coatings, that is coatings with a thickness greater than about 60 or more preferably greater than about 80, or still more preferably greater than about 100 microns in thickness. The additive can improve the heat resistance of a powder coating composition by at least about 20%. The heat resistance is measured by the tape pull test. The improvement in heat resistance can be manifested either as the ability to maintain integrity at higher temperatures for a set period of time, or the ability to maintain integrity at a set temperature for longer time periods. This composition further provides abrasion resistance and electrical resistance. It can be particularly useful for coating high temperature stacks, mufflers, manifolds, boilers, ovens, furnaces, steam lines, heat exchangers, barbecue equipment, cooking utensils and other parts that require a high heat resistance powder coating compositions.

The heat resistant polymeric coating compositions of the present invention can be coated onto a substrate which displays 0% crosshatch adhesion failure after 2 hours at 540°C, said coating comprising:

- a) the reaction product of:
 - i) glycidyl-functional polyacrylic polymer; and a
 - ii) hydroxyl-functional polysiloxane; and

- b) at least one inorganic oxide particle or metal particle.

One aspect of the invention is directed to a heat resistant coating composition comprising :

- 5 a) at least one glycidyl-functional polyacrylic polymer;
 b) at least one hydroxyl-functional polysiloxane;
 c) at least one inorganic compound selected from the group consisting of
 silicates, hydrates of silicates, metasilicates and mixtures thereof;
 d) at least one ceramic material selected from the group consisting of a metal
 oxide, a metal and mixtures thereof; and

10 The coating composition can be heated to form a continuous film having a
thickness greater than about 45 microns. The coating formed has good thermal resistance
at temperatures of from about 370°C to about 540°C, based on the tape pull test,
depending on the thickness of the film.

15 The present invention is further directed to heat resistant protective coating
compositions comprising:

- a) at least one glycidyl-functional polyacrylic polymer;
 b) at least one hydroxyl-functional polysiloxane;
 c) at least one inorganic compound which is not an inorganic oxide;
 d) an inorganic oxide or metal or mixture of inorganic oxide and metal; and
20 e) an optional flow control agent,

wherein said composition can be heated to form a continuous film having a
thickness greater than about 45.

25 Specifically, the at least one inorganic compound can be silicates, hydrates of
silicates, metasilicates and mixtures thereof. These coatings have excellent heat resistant
characteristics and pass the tape pull test after about 4 and 24 hours at temperatures up to
about 530°C (about 1000°F) as compared to the compositions without component d
additives, which displayed good thermal endurance to temperatures of about 340°C to
about 395°C after about 4 and 24 hours.

30 The present invention is also directed to articles comprising at least one substrate,
and present on at least one surface of the substrate is a composition comprising:

- a) the reaction product of:
 i) at least one glycidyl-functional polyacrylic polymer; and

- ii) at least one hydroxyl-functional polysiloxane;
- b) of at least one inorganic compound which is not an inorganic oxide;
- c) at least one inorganic oxide or metal; and
- d) at least one optional adhesion promoter.

5

In another aspect, the invention discloses a method for the preparation of heat resistant protective coatings comprising the steps of:

- a) providing a dry blend of powder-based materials comprising:
 - i) at least one glycidyl-functional polyacrylic polymer;
 - 10 ii) at least one hydroxyl-functional polysiloxane;
 - iii) at least one inorganic compound which is not an inorganic oxide;
 - iv) at least one inorganic oxide or metal (including mixtures of inorganic oxides and metals); and
 - v) an optional flow control agent,
- 15 b) melt mixing said blend and cooling to form solid particulate;
- c) grinding said particulate to form a powder-based composition wherein said composition comprises an average particle size less than about 150 microns; and
- 20 d) coating said composition on a substrate and heating to a temperature greater than about 190°C or greater than about 205°C.

In all aspects of the invention, an adhesion promoter can also be present in the coating composition.

25 Detailed Description Of The Invention

The protective coatings of the present invention are characterized as having increased heat resistance properties and are substantially free of coating defects, especially at high film thickness. The coatings are particularly useful on articles which are subjected to elevated temperatures including stacks, mufflers, manifolds, boilers, 30 ovens, furnaces, steam lines, heat exchangers, barbecue equipment and cooking utensils. Furthermore, a benefit of being able to apply this coating at a high film build is to accommodate the variety of geometrical shapes of different articles and to allow for

variations in manual spraying of the powder coating composition. These coatings exhibit substantially no pitting.

The compositions of the present invention comprise a silicone resin, in a range from about 5.0% by weight to about 40.0% by weight, and preferably from about 10.0% by weight to about 30.0% by weight, based on the total composition solids. The silicone resin can be any alkyl and/or aryl substituted polysiloxane, copolymer, blend or mixture thereof, the alkyl substitution preferably selected from alkyl groups of 1 to 4 carbon atoms, more preferably 1 to 3 carbon atoms, and most preferably methyl, propyl and the aryl substitution most preferably comprising phenyl groups. The silicone resins are heat stable, preferably they do not decompose up to at least 316°C (600°F) when exposed for 90 hours. More preferably they will not decompose when subjected to ambient environmental conditions (e.g., in the presence of air) at 343°C (650°F) for two weeks.

The silicone resins useful in the practice of the present invention comprise silicone polymers, such as those prepared from organochlorosilanes (such as methyltrichlorosilane, phenyltrichlorosilane and dimethylchlorosilane), and commercially available materials such as phenylsilicone Silres® 601 or methylsilicone MK, available from Wacker Silicone, Adrien, MI.), and propylphenyl Z-6018 or methylphenylsilicone 6-2230 available from Dow Corning, etc. Suitable resins are also described in U.S. patent Nos. 3,585,065, 4,107,148, 3,170,890 and 4,879,344, incorporated herein by reference.

Preferably, a hydroxyl-functional polysiloxane is used, with the hydroxyl-functionality up to about 10% by weight, preferably in a range from about 0.5% by weight to about 10.0% by weight, more preferably from about 1.0% by weight to about 15.0% by weight, and most preferably from about 5% to about 15% by weight based on the total polysiloxane solids. The compositions may include hydroxyl-functional organo-siloxanes, said organo-siloxane comprises units, including dimethyl, diphenyl, methyl-phenyl, phenylpropyl and their mixtures. Examples of commercially available hydroxyl-functional polysiloxanes include Dow Corning® 1-0543, Dow Corning® 6-2230 and Dow Corning® Z-6018 from Dow Corning (Midland, MI); Wacker Silres® MK and Wacker Silres® 601 from Wacker Silicone Corp., (Adrien, MI); General Electric SR-355 from General Electric (Waterford, NY); and PDS-9931 from Gelest, Inc., (Tullytown, PA). Other suitable silicone-based polymers include those described in U.S. Patent No.

4,107,148 (Fujiyoshi et al.) and U.S. Patent No. 4,879,344 (Woo et al.), incorporated herein by reference. Said polymers can self-condense and/or react with glycidyl functional polymers to form a crosslinked network.

Acrylic polymers are also present in the powder-based compositions, and they are preferably glycidyl-functional polyacrylic polymers. These glycidyl functional acrylic resins act as curing agents. Suitable resins include at least about 5 wt-% to about 100 wt-% glycidyl functionality. These curing agents aid in the curing of the powder coating composition and also, can substantially reduce the condensation reaction which has troubled the prior art. Examples of commercially available glycidyl-functional polyacrylic polymers include Fine-Clad™ A-244A from Reichold Chemicals, Inc. (Research Triangle Park, NC), and Almatex PD-7690 from Anderson Development Company (Adrain, MI). Said polymers may react with hydroxyl-functional compounds, through an addition mechanism, to form a crosslinked network. Typically a glycidyl-functional acrylic resin is present in an amount effective to allow curing and substantially reduce the condensation of the reaction, preferably in a range from about 1.0% by weight to about 20.0% by weight, and preferably from about 3.0% by weight to about 15.0% by weight, based on the total composition solids. Generally the reaction between the hydroxyl functional resin and the glycidyl functional curing agent is an addition reaction; however, there may be some amount of condensation that occurs between silanol groups which can be tolerated. It will be understood by one of skill in the art that the more glycidyl-functionality in the acrylic resin, the less condensation occurs.

Inorganic compounds are present in the powder-based compositions in a range from about 10.0% by weight to about 70.0% by weight, and preferably from about 20.0% by weight to about 40.0% by weight, based on the total composition solids. The preferred inorganic compounds are hydrated silicates of aluminum (mica), calcium metasilicate (wollastonite) and their mixtures. Commercially available pigments include Micro Mica® C-3000 from KMG Minerals (King Mountain, NC) and Nyad® 325 from Nyco (Willsboro, NY). It is surmised that the inventive coating unique heat resistant properties can be attributed, in-part, to said compounds. For example, it is known that inorganic compounds are often used as fillers to increase the coatings volume and economics. Surprisingly, the present inventors have discovered that mica and

wollastonite significantly increase the coating heat resistance properties. Inorganic fillers such as zinc oxide, zinc borate, barium sulfate, calcium sulfate, calcium carbonate, hydrated silicate of magnesium and anhydrous sodium potassium alumina silicate fail to increase the coatings heat resistance properties. It is further surmised that mica and
5 wollastonite enhance the glycidyl-silanol addition reaction to form a substantially crosslinked network. In addition, these inorganic compounds are especially needed for white coatings. These inorganic compounds preferably have average particle sizes of from about 5-100 microns, more preferably 5-60 microns and most preferably 5-40 microns.

10 When ceramic materials such as inorganic metal or semimetal oxides and metals are added to a powder coating composition, such as ones described in U.S. Patent No. 5,684,066, incorporated herein by reference, the thermal endurance of the coating (its ability to withstand high temperatures for extended periods of time) is significantly improved. It is surprising that even a coating which already displays high temperature
15 endurance because of the addition of a unique selection of silicates can have its thermal resistance properties even further improved by the addition of this class of compounds. Some oxides, e.g., zinc oxide, were found to not significantly improve the thermal properties of the composition without the silicates present. The preferred materials of this class include, but are not limited to, inorganic oxides such as aluminum oxide, titanium
20 oxide, chromium oxide, zirconium oxide, cesium oxide, magnesium oxide, iron oxide, mixed oxides (e.g., BaO/TiO₂, CaO/SiO₂, 2CaO/SiO₂, CaO/TiO₂, MgO/TiO₂, 2SiO₂/3Al₂O₃, etc. Other inorganic oxides include tin oxides, nickel oxides, barium oxide, lead oxide, copper oxides, magnesium oxide and the like, especially inorganic oxides which can fuse or coalesce at temperatures above 425°C or above 480°C to form
25 ceramic materials. Metals which are preferred in the practice of this invention are the metals which may be used to form the inorganic oxides listed above, particularly those metals whose oxides form ceramics when heated above 425°C or 480°C (such as aluminum, zirconium, chrome, titanium and the like). This preference for these metals may be indicative of a reaction of the metals with oxygen present in the system (e.g.,
30 bound oxygen) to form a fused or bound metal oxide link to the hydroxyl-functional siloxane or other inorganic oxides or silicates within the system or to the substrate. The inventors are not bound by this hypothesis, but gratuitously offer it as a possible

suggestion for a basis of selecting metals for the practice of this aspect of the present invention. Mixtures of inorganic oxides, mixtures of metals and mixtures of inorganic oxides and metals may be used in the practice of the present invention, and the concentration of these materials within the powder-based coating composition may range
5 from about 1%, 10% or 20% by weight in the powder-based coating composition up to about 50%, 60% or 70% by weight in the powder-based coating composition. A preferred concentration in the practice of the present composition may be about 4% by weight to about 45% by weight or about 8% by weight to about 40% by weight of the total composition.

10 The metals and/or inorganic oxides are preferably added as particulate materials, usually of a size range between about 0.05 to about 100 microns, more preferably between about 0.05 and about 50 microns, and still more preferably between about 0.1 and about 10 microns.

As discussed above, the ceramic materials can increase the heat resistant
15 temperature of a powder coating composition by at least about 20%, more preferably by at least about 30%. This improvement is evident at low film thickness as well as high film thickness.

Flow control agents optionally can be present in the powder-based compositions in a range from 0% to from about 0.2% by weight to about 3.0% by weight, and
20 preferably from about 0.5% by weight to about 1.5% by weight, based on the total composition solids. The flow control agents may include acrylics, silicones and fluorine-based polymers. Examples of commercially available flow control agents include Resiflow P-67⁸ and Clearflow Z-340⁸ from Estron Chemical, Inc. (Calvert City, KY); Mondaflo⁷ 2000 from Monsanto (St. Louis, MO); Modarez⁷ MFP from Synthron, Inc.
25 (Morgantown, NC); and BYK⁷ 361 from BYK Chemie (Wallingford, CT). Said agents enhance the compositions melt-flow characteristics and help eliminate surface defects.

The powder-based compositions may contain additives including adhesion promoters, degassing agents, catalysts, fillers, texturizers, coloring agents, plasticizers, surfactants and their mixtures.

30 If desired, adhesion promoters can be used in the powder-based compositions including epoxy-based polymers, silane-based polymers, phenolic resins, chlorinated polyolefins and their mixtures. Examples of commercially available adhesion promoters

include Araldite⁷ GT-7013 and Araldite⁷ GT-7220 from Ciba-Geigy corporation (Hawthorn, NY). The adhesion promoters may be present as 0% by weight or in a range from about 0.1% by weight to about 20.0% by weight, and preferably from about 0.1% by weight to about 15.0% by weight, based on the total composition solids. It has been
5 found in the practice of the present invention that such materials as boron carbide (B_4C), boron nitride, Cr_3C_2 (chromium carbide), $CrSi_2$, HfB_2 , HfC , $HfSi_2$, $MoSi_2$, NbC , CaF_2 , LiF , TiC , $LiCl$, MgF_2 , Si_3N_4 , and the like can provide good additional properties to the composition and the coating. Boron carbide in particular improves certain adhesion or coating properties.

10 Degassing agents can be used in the powder-based compositions and may be present as 0% by weight or in a range from about 0.1% by weight to about 5.0% by weight, and preferably from about 0.5% by weight to about 3.0% by weight, based on the total composition (e.g., solids). Examples of commercially available degassing agents include Uraflow B from GCA Chemical Corporation (Brandenton, FL), Oxymelt A-2⁸
15 from Estron Chemical (Calvert City, KY), and Benzoin from Generichem Corp. (Little Falls, NJ). Said materials assist in the release of gases during the curing process.

Small quantities of catalysts may be used in the powder-based compositions which may include stannous octoate, dibutyl tin dilaurate, zinc octoate and their mixtures. Commercially available catalysts include Octaflow ST-70⁹ from Estron
20 Chemical, Inc., (Calvert City, KY) and Actiron DBT⁹ from Synthron (Morgantown, NC). The catalysts may be present in a range from about 0.01% by weight to about 5.0% by weight, and preferably from about 0.1% by weight to about 3.0% by weight, based on the total composition solids. The catalysts are used to enhance the curing characteristics of the powder-based compositions.

25 If desired, other inorganic fillers can be used in combination with the preferred inorganic compounds of the present invention. Suitable examples include zinc oxide, magnesium silicate (Talc), calcium sulfate, barium sulfate, zinc borate, anhydrous sodium potassium alumino silicate, calcium sulfate, calcium carbonate and their mixtures. A commercially available filler is Duramite⁷ from ECC International (Atlanta,
30 GA). The fillers may be present in a range from about 10.0% by weight to about 50.0% by weight, and preferably from about 20.0% by weight to about 40.0% by weight, based on the total composition solids. The fillers can be used to provide texture, control gloss

and increase the coatings volume to enhance its economics.

If desired, texturizers can be used in the powder-based compositions and include polytetrafluoroethylene, rubber, glass grit, talc and their mixtures. A commercially available texturizer includes Shamrock SST-3 from Shamrock Technologies (Newark, NJ). The texturizer may be present in a range from about 1.0% by weight to about 10.0% by weight, and preferably from about 2.0% by weight to about 7.0% by weight, based on the total composition solids.

Coloring agents can be used in the powder-based compositions and any heat stable coloring agent may be used. The preferred coloring agents are carbon black and black mixed metal oxides. Commercially available coloring agents include Black No. 101 from the Shepard Color Company (Cincinnati, OH), and Special Black 100 from Degussa AG (Frankfurt, Germany). The coloring agent may be present in a range from about 1.0% by weight to about 25.0% by weight, and preferably from about 5.0% by weight to about 15.0% by weight, based on the total composition solids.

Preferably, the adhesion promoter is present from about 0.01% by weight to about 10% by weight of the polymer content of the composition, more preferably from about 0.5% by weight to about 5% by weight, most preferably from about 1% by weight to 5% by weight, to increase initial adhesion and reduce cross-hatch adhesion failure to less than 5%. Cross-hatch adhesion failure is tested by scoring a grid of 5 x 5 lines spaced about 2mm apart, applying an acrylate pressure sensitive adhesive tape on a polyester backing against the crosshatching, and quickly removing the tape by pulling at an angle of about 90 degrees. The number of squares of coating which have been removed are then measured. By reducing the cross-hatch adhesion failure (after melting and curing of the silicone resin composition) to less than 5%, a polymeric additive is identified as an adhesion promoter. It has been surprising in the practice of the present invention that typical polymeric additives conventionally used as adhesion promoters (e.g., bisphenol A epoxy resins, Novolac-modified bisphenol A, resols, polyethylene, polypropylene, silane resins, phenolic resins with chlorinated polyolefins and polyethylene terephthalate) did not perform according to the present definition of adhesion promoters or adhesion enhancers.

The useful adhesion promoters of the present invention are, as previously noted, determinable by the test procedures described below. From a compositional standpoint,

the preferred chemical classes of adhesion promoters comprise (meth)acrylic polymers and copolymers, including ambifunctional or polyfunctional (meth)acrylic polymers and copolymers, as homogeneous or heterogeneous compositions, blends, mixtures or melts. The term "(meth)acrylic" is used to encompass both acrylic and methacrylic resins.

- 5 Acrylate polymers (including copolymers) derived from acrylic acid, methacrylic acid, acrylic anhydride, n-butyl acrylate, n-butyl methacrylate, methyl acrylic acid, methyl methacrylic acid, isobutyl acrylic acid, isobornyl (meth)acrylate, decyl acrylate, lauryl (meth)acrylate, trimethylsilyl(meth)acrylate, methacryloxypropyltrimethoxysilane, fluorinated acrylates (such as those described in U.S. patent No. 5,397,669) and the like
10 are most preferred. Copolymers of these (meth)acrylates, or blends or mixtures of (meth)acrylates as with olefinic resins (e.g., polyethylene and polypropylene), vinyl ethers (butyl vinyl ether, propyl vinyl ether, etc.), vinyl esters (e.g., vinyl acetate), styrenes (e.g., 4-methylstyrene, styrene, alpha-methylstyrene) are also highly preferred. The more preferred promoters comprise methacrylic or acrylic acid (anhydrides or
15 alkylacrylic acid) copolymers with ethylenically unsaturated comonomers, particularly olefinic copolymers (ethylene, propylene, styrene, butadiene, etc.) which, by themselves, form linear polymer chains. Ethylene-acrylic acid copolymers such as PrimacorTM 5990 Polymer are the most preferred.

- High cure temperatures are normally needed for curing to produce coatings with
20 improved initial adhesion. Temperatures of at least 280°C, and as high as 550°C are usually employed. Even at these high curing temperatures, some prior coatings still do not have cross-hatch failures of less than 5%. It is therefore surprising that coating compositions of the present invention can be cured at temperatures of less than about 230°C, substantially lower than normally used, to produce coatings having cross-hatch
25 failures of less than 5%, through the incorporation of adhesion promoters.

- Plasticizers may be used in the present invention to provide flexibility. Plasticizers may include polymeric resins, elastomers, waxes, oils and their mixtures. The plasticizers may be present in a range from about 1.0% by weight to about 15.0% by weight, and preferably from about 5.0% by weight to about 10.0% by weight, based on
30 the total composition solids.

Surfactants can be used and may include inorganic polyphosphates, organic polyacids, nonionic block copolymers and their mixtures. The surfactants may be

present in a range from about 0.5% by weight to about 3.0% by weight, and preferably from about 1.0% by weight to about 2.0% by weight, based on the total composition solids. The surfactants are useful as dispersing agents for the inorganic compounds and inorganic fillers.

5 Fluidizing agents can be used to improve the dry-flow characteristics of the powder-based compositions. Examples include fumed silica, alumina oxides and their mixtures. The fluidizing agent can be present in a range from about 0.05% by weight to about 1.0% by weight, and preferably from about 0.1% by weight to about 0.5% by weight, based on the total composition solids.

10 In the inventive method, for the preparation of heat resistant protective coatings, the powder-based materials are combined and agitated to form a dry blend. The blend is melt mixed in an extruder, at a temperature less than about 130°C, and cooled to form solid particulate. Fluidizing agents may be added at this stage of the process to enhance the materials dry-flow characteristics. Preferably, the particulate is ground at a
15 temperature less than about 20°C. Lower temperatures reduce melt coagulation and enhance the grinding process. The powder-based compositions can have an average particle size in a range from about 0.1 microns to about 500 microns and preferably from about 30 microns to about 200 microns. Said compositions may be applied on a substrate through electrostatically spraying or with a fluidized bed method. The coated
20 substrate is then heated to a temperature in a range from about 180°C to about 250°C, and preferably from about 190°C to about 240°C, and more preferably from about 200°C to about 225°C. It is generally known that elevated temperatures can accelerate a material's reactivity. For example, a reference describing the frequency of bond formation is described in A Organic Chemistry, T.W. Graham Solomons, second edition, pages 139-
25 141. Briefly, the collision theory of reaction rates describes how the rates of chemical reactions are directly proportional to the collision frequency. In the present invention, it is surmised elevated temperatures increase the frequency and extent of addition and/or condensation reactions to form a crosslinked polymer matrix.

 The protective coatings can have a film thickness in a range from about 25
30 microns to about 255 microns, and preferably from about 45 microns to about 200 microns. A higher-film-build can enhance the coating and increase the protective value of the coatings with a greater film thickness that provides an extra barrier of protection.

For example, during manual and automated spraying applications it is often necessary to deposit a high-film-build to assure a complete deposition of the particles on the substrate. Additionally, a protective coating comprising a film thickness greater than about 100 microns is preferred in that such a high-film-build can enhance the coatings resistance to abrasion and environmental corrosives.

The protective coatings provide excellent heat resistant properties and are particularly useful on articles which are subjected to elevated temperatures including stacks, mufflers, manifolds, boilers, ovens furnaces, steam lines, heat exchangers, barbecue equipment and cooking utensils.

The tape pull test used to measure heat resistance is described below and was run at 530°C. This is a very severe test and as mentioned before, the samples that passed this test are much preferred, though the ones that failed at 530°C are also included in the present invention if they improve their heat resistances by at least about 20% through the addition of the metal, metal oxides or mixtures thereof. Preferably, the improvement is at least about 30%, more preferably at least about 50%. Also, as discussed above, the improvement can be either maintaining integrity at a higher temperature for a set period of time, or at a set temperature for longer amounts of time, with the most desirable being an increase in both temperature and time over compositions without the addition of metal, metal oxides or mixtures thereof.

The present invention is further illustrated, but not limited to, the following examples.

Examples

The following test methods were used:

25

Tape Pull Test Method (TPTM)

Aluminum cast coupons were electrostatically sprayed with powder-based compositions and heated in an electric oven for 15 minutes at 204°C. The samples were subjected to a temperature of 530°C (about 1000°F) and tested at about 4 and 24 hours. Other temperatures can be used, as appropriate. After heating, the samples were cooled to ambient room temperature and aged for at least one hour. The samples were then covered with a piece of Scotch⁷ Brand A8919≅ tape from 3M Company (St. Paul, MN)

and firmly applied using hand pressure. The tape was quickly removed, using a 90° peel mode, and visually inspected for signs of coating failure. The protective coating passes the TPTM when said coating is not transferred to the tape.

5 **Examples 1-3 and 4-C**

In the following examples of the present invention, some of the following materials and their abbreviations are used.

Dow Corning 1-0543 Resin is a silicone comprising a mixture of Dimethyl-, Diphenyl-, Methyl-, and Phenyl- Silicone moieties.

10 A-244-A(GMA) is a glycidyl functional (meth)acrylic polymer

Z-6018 is a silicone resin having a mixture of Phenyl- and Propyl- Silicone moieties,

P-67 is an Acrylic Polymer/Silicon resin mixture

Uraflow B is Benzoyl Phenyl Carbinol

15 ST-70 is a Stannous Octoate

SST-3 is a Polytetrafluoroethylene

NYAD 325 is Calcium Metasilicate

Black 1G is Copper Chromate

Aluminum 1663 is a dedusted Aluminum Flake

20 ZrO₂ is Zirconium Oxide

Boron Carbide is boron carbide

25 The compositions of the examples are tabulated in Table I below and the results of Pull-Tape Test tabulation in Table II. They are made in the conventional manner for powder coating.

TABLE I

Raw Materials	1	2	3	4-C
Dow Corning Z-10543	50.0	50.0	50.0	50.0
Z-6018 Intermediate	30.0	30.0	30.0	30.0
Fine-clad A-244-(GMA)	20.0	20.0	20.0	20.0
Resiflow P-67HBF	1.4	1.4	1.4	1.4
Ultraflow B	1.0	1.0	1.0	1.0
Octaflow ST-70	1.0	1.0	1.0	1.0
Shamrock SST-3	0.5	0.5	0.5	0.5
NYAD 325 Wollanstonite	110.0	110.0	80.0	100.0
Vicron 41-8 Limestone	-	-	-	60.0
Black 1G	30.0	30.0	30.0	30.0
Aluminum 1663	20.0	-	-	-
ZrO ₂ (reactor grade)	-	80.0	60.0	-
Boron Carbide	-	-	25.0	-

5

TABLE II

TPTM	1	2	3	4-C
4 Hours	Pass	Pass	Pass	Fail
24 Hours	Pass	Fail	Pass	Fail

10

Examples 5 - 9

The following powder-based compositions, using various inorganic oxides or metals, were also made in the conventional manner and evaluated using the tape pull-test method (TPTM) listed above. The ones that failed are not as desirable as the ones that passed, but as mentioned before, the test was conducted under very severe conditions and therefore the failed examples in this set are still considered part of the broader invention.

	Dow Corning® 1-0543	50.0 grams
	Fine-Clad™ A-244-A	20.0 "
10	Dow Corning® Z-6018	30.0 "
	Resiflow P-67™	1.4 "
	Uraflow B	1.0 "
	Octaflow ST-70	1.0 "
	Shamrock SST-3	0.5 "
15	NYAD 325 Wollanstonite	110.0 "
	Black 1G	30.0 "

Example	Pigment	Grams	TPTM (530°C)
5	Silica-Alumina Ceramic	81.3	Fail < 4 Hours
6	Alkali Alumina Ceramic	81.3	Fail < 4 Hours
7	Aluminum Oxide A-10	81.3	Fail < 4 Hours
8	Aluminum Oxide A-152	81.3	Fail < 4 Hours
9	Boro-Silicate	81.3	Fail < 4 Hours

What We Claim:

1. A powder-based coating composition comprising:
 - a) at least one polyacrylic polymer;
 - b) at least one hydroxyl-functional polysiloxane;
 - 5 c) at least one inorganic compound selected from the group consisting of silicates, hydrated silicates, metasilicates and mixtures thereof;
 - d) an inorganic oxide or metal; and
 - e) an optional flow control agent.
- 10 2. The coating composition of Claim 1 wherein said composition is heated to form a continuous film having a thickness greater than about 45 microns.
3. The coating composition as described in Claim 1, wherein said coating is characterized as having a film thickness in a range of from about 45 microns to
15 about 200 microns.
4. The coating composition as described in Claims 1, 2 or 3 wherein said polyacrylic polymer is a glycidyl-functional polyacrylic polymer.
- 20 5. The coating composition as described in any of Claims 1 - 4 wherein the flow-control agent is present in a range from about 0.05% by weight to about 3.0% by weight.
- 25 6. The coating composition as described in any of Claims 1 - 5, wherein said inorganic compound is present in a range from about 10% by weight to about 70% by weight.
- 30 7. The coating composition of any of the preceeding Claims wherein said inorganic oxide is selected from the group consisting of titanium oxide, zirconium oxide, aluminum oxide and chromium oxide and said metal is selected from the group consisting of aluminum, chromium, zirconium and titanium.

8. The coating composition of any of the preceeding Claims wherein said inorganic oxide or metal, by itself, will form a ceramic material when heated above 900°C.
9. The coating as described in any of Claims 2 - 8 wherein said coating is substantially free of coating defects and passes the tape pull test method after about 2 hours at 540°C.
10. A powder based coating composition comprising:
- a) the reaction product of:
 - i) at least one glycidyl-functional polyacrylic polymer; and
 - ii) at least one hydroxyl-functional polysiloxane;
 - b) of at least one inorganic compound which is not an inorganic oxide;
 - c) at least one inorganic oxide or metal; and
 - e) at least one optional adhesion promoter.
11. An article comprising at least one substrate and coated on at least one surface of the substrate is a heat resistant protective coating composition of Claim 10, wherein said coating is characterized as having a film thickness greater than about 45 microns.
12. The article as described in Claim 11, wherein said coating is substantially free of coating defects and passes the tape pull adhesion method after about 2 hours at 540°C.
13. The article of Claim 11 or 12 further comprising an adhesion promoter.
14. A method for the preparation of heat resistant protective coatings comprising the steps of:
- A) providing a dry blend of powder-based materials comprising:
 - a) the reaction product of :
 - i) at least one glycidyl-functional polyacrylic polymer; and
 - ii) at least one hydroxyl-functional polysiloxane;

- b) at least one inorganic compound which is not an inorganic oxide or metal;
- c) an inorganic oxide or metal; and
- d) an optional flow control agent;
- 5 B) melt mixing said blend and cooling to form solid particulate;
- C) grinding said particulate to form a powder-based composition having an average particle size of less than about 150 microns; and
- D) coating said composition onto a substrate and heating to a temperature greater than about 180°C.
- 10
15. The method as described in Claim 14, wherein said materials are dry blended at ambient room temperatures.
16. The method as described in Claim 14 or 15, wherein the melt mixing process is accomplished at a temperature less than about 130°C.
- 15
17. The method as described in any of Claims 14 - 16, wherein the grinding process is accomplished at a temperature less than about 20°C.
18. The method as described in any of Claims 14 - 17, wherein said composition is coated onto a substrate by electrostatically spraying.
- 20
19. The method as described in any of Claims 14 - 18, wherein said protective coating is characterized as having a film thickness greater than about 45 microns.
- 25
20. A powder coating composition comprising a ceramic additive, wherein said additive increases the heat resistance by at least about 20%, as measured by the tape pull test, when compared to a powder coating composition without the ceramic additive.
- 30
21. The powder coating composition of Claim 20 further comprising an inorganic compound selected from the group consisting of silicates, hydrated silicates,

metasilicates and mixtures thereof.

22. The powder coating of Claim 21 wherein said silicate is selected from the group consisting of hydrated aluminum and calcium.

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23. The powder coating of any of Claims 20 - 22 wherein said ceramic additive is selected from the group consisting of metal, metal oxides and mixtures thereof.

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24. The powder coating composition of any of the preceeding Claims further comprising an adhesion promoter.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/00197

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D5/03 C09D133/04 C09D183/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 22728 A (FULLER H B CO) 26 June 1997 see claim 1 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9722728 A	26-06-1997	US 5684066 A	04-11-1997
		CA 2236981 A	26-06-1997
		CN 1201476 A	09-12-1998
		EP 0865469 A	23-09-1998
		NZ 324195 A	25-02-1997
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